

Potential-Induced Structure Transitions in Self-Assembled Monolayers: Ethanethiol on Au(100)

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Self-assembled monolayers (SAMs) of alkanethiols on Au(111) have been studied extensively in UHV, in air and in an electrochemical environment [1,2]. In the latter case, the structure of the SAMs was determined in-situ by scanning tunnelling microscopy, whereas cyclic voltammetry and double-layer capacity measurements were employed for characterization of the electrochemical properties, such as the blocking power for electron transfer. Experiments with short-chain alkanethiols revealed a surprisingly high mobility on Au(111), e.g., reflected in potential-induced order-disorder transitions [3]. Similar studies for Au(100) electrodes are practically non-existent, although the use of different surface crystallographic orientations should shed light on the role of the substrate in determining the structure of the SAM. Studies with Au(100) in UHV have been reported [4,5,6].

In the following we report first results from a structure study of ethanethiol SAMs on Au(100) in sulfuric acid. The flame-annealed Au(100) electrode is reconstructed before modification in a 1 mM ethanolic solution of the thiol. Adsorption of the latter lifts reconstruction and after a modification time of about 12-16 h, 25% of the surface are covered by monoatomic high, rectangularly shaped gold islands formed by the surface excess of the hex-reconstruction. Quite remarkable, the monoatomic deep vacancy islands (VIs) which are routinely observed on alkanethiol-modified Au(111) surfaces, are completely absent for Au(100).

Immersion of the ethanethiol-modified Au(100) electrode into the electrolyte under potential control yields two markedly different structures of the SAM, depending on whether the potential is positive (here +0.55 V vs. SCE) or negative (here -0.15 V vs. SCE) of +0.3 V vs. SCE. Both structures reveal a quadratic arrangement of the molecules, the molecular squares being rotated by 45° in both cases with respect to the main axes of the substrate. However, besides domains of ordered SAMs, a considerable fraction of the surface shows disorder, a more detailed structural characterization of which being not possible with STM. At +0.55 V, a stripe structure is observed in STM (Fig.1a), with a next-neighbor distance of 4.8 ± 0.5 Å and every 6th or 7th row lying 0.6 Å deeper than the molecules inside the stripes.

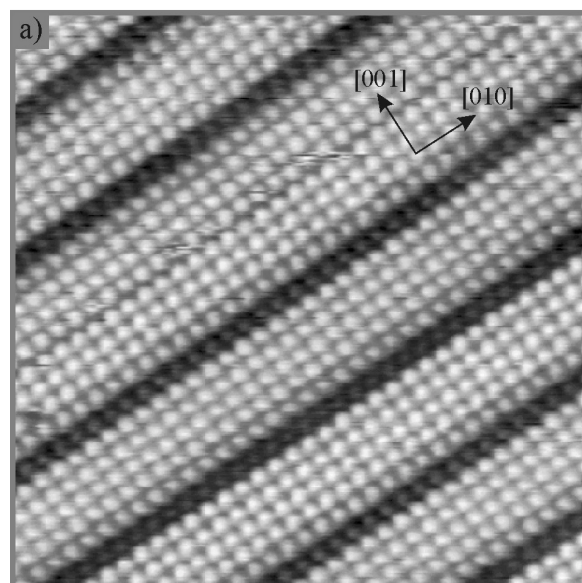
At -0.15 V a patched structure is found for the SAM (Fig. 1b), the molecules in the patches being again 0.6 Å deeper than outside. In addition, the surface fraction of Au(100), covered by monoatomic high gold islands has increased beyond the expected 25% to values between 40 and 50%. The next-neighbor distance is 4.4 ± 0.5 Å. Potential steps from one structure region to the other causes a transition between striped and patched structure. In addition to this structure transition monoatomic deep holes (here VIs) are created when the potential is stepped from the cathodic to the anodic region, which cover about 14% of the total surface. The potential-induced structure transition is remarkably reversible, which testifies to the high surface mobility of the thiolate moiety.

At present, we cannot give a full account of the SAM structures, e.g., identifying the adsorption sites for these incommensurate superstructures. An important piece of information, however, may be derived from the high island fraction of the patched structure, which suggests that an extra amount of gold atoms has been expelled onto the surface due to a potential-driven expansion of the SAM-covered gold lattice. We are led to conclude that the mobile species on the surface is gold thiolate rather than the ethanethiol proper. As a consequence, the surface density of gold atoms changes drastically with a structural change of the SAM, the latter being unequivocally derived from STM measurements.

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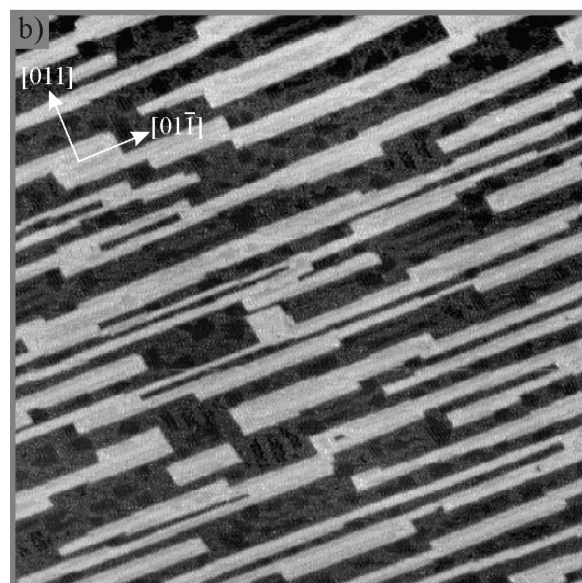
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10 x 10 nm²



$E_{\text{SCE}} = +0.55$ V

90 x 90 nm²



$E_{\text{SCE}} = -0.15$ V

Fig.1: STM images of ethanethiol-modified Au(100) in 0.1 M H₂SO₄, immersed at two different electrode potentials.